

## CHARACTERIZATION OF THE CHANGES OF COLOUR AND SOME WOOD COMPONENTS ON THE SURFACE OF STEAMED BEECH WOOD

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### ABSTRACT

The aim of this work was to explain the changes in the structure of the main wood components, which cause the colour changes on the surface of the steamed beech wood.

The results obtained from the measurement of the surface colourity of the steamed beech wood showed that the steaming under the given conditions had influence on the change of the colourity what was reflected in the change of the total crystallinity index -  $A_{1370}/A_{2900}$  and another important ratios:  $A_{1332}/A_{1316}$ ,  $A_{1370}/A_{1504}$  and  $A_{1736}/A_{1640}$ . The obtained results showed that the steaming of beech wood resulted in the colour change of the surface, which was accompanied by the changes in the chemical characteristics of the main components of wood (cellulose, hemicelluloses and lignin).

The colour changes of beech wood due to the steaming were the result of the complex chemical changes of the wood components. The steaming under the given conditions caused the partial degradation of hemicelluloses and amorphous cellulose regions and increase in the crystallinity of cellulose. It was accompanied with the concomitant release of lignin-carbohydrate bonds in the surface layers of wood, which was reflected in subsequent removal of the easily degradable polysaccharides and in the relative increase of the lignin content.

**Key words:** beech wood, steaming, colour, ATR-FTIR spectroscopy, degradation of polysaccharides, total crystallinity index (TCI).

### INTRODUCTION

Steaming of wood is an inseparable part of the technological wood processing in sawmills, veneer and plywood factories, in the production of bentwood furniture and for other wood processing (SERGOVSKI 1968, NIKOLOV *et al.* 1980, SETNIČKA 1989, TREBULA and KLEMENT 2005).

It is a hydrothermal treatment in which the wood is treated with water respectively with water vapour at different modes - temperature, pressure, time and hydro module (ŠŤŤÝ 1982, LAWNICZAK 1995, DZURENDA and DELIISKI 2000), carrying out a change in the external and internal characteristics of wood, which may be permanent or temporary.

The most important transition change is plasticity, which is related to the temporary reducing of the mechanical strength and flexibility. The permanent changes include changes in the chemical composition, structure and colouration. These changes subsequently result in a higher dimensional stability (BEKHTA and NIEMZ 2003, ESTEVES *et al.* 2007), decrease

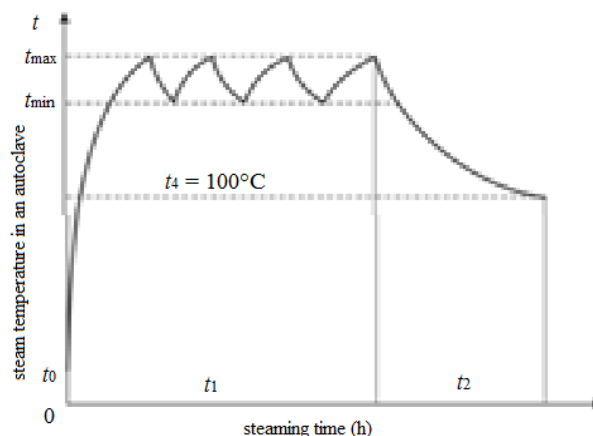
in sorption properties with respect to water vapour (METSÄ-KORTELAJAINEN *et al.* 2006) and sometimes they cause an increase in the biological stability and also suitable discolouration of wood. An undesired change is a loss of strength, weight loss and in some cases increase in shrinkage (SOLÁR 1997).

Using of the hydrothermal treatment for the desired colour shade of wood is closely linked to the chemical changes that occur during the mating (KAČÍK 1997, TOLVAJ *et al.* 2010). The authors SOLÁR (1997) and HALAJ *et al.* (2001) in their works showed that the colour changes that occurred as a result of hydrothermal treatment were related to the chemical changes of lignin and the reactions of degradation products of polysaccharides and extractives. SOLÁR and KAČÍK (1995) demonstrated the colour change of lignin alone from pale cream to the cinnamic colour in consequence of time and temperature as a result of new chromophore groups. LAUROVÁ *et al.* (2004) reported the discolouration of beech wood as a result of the steaming from bright grey - pale yellow to dimly red. The similar colour changes of the surface of beech after a hydrothermal treatment by the steaming, respectively by the drying, are presented in the works of many other authors too (DZURENDA 2013, TOLVAJ *et al.* 2012, DZURENDA and DELIISKI 2012, KLEMENT and MARKO 2009, BABIAK *et al.* 2004, MOLNAR and TOLVAJ 2002).

The aim of this work was to characterize the colour changes on the surface of the steamed beech wood as a result of the changes in the structure of the main wood components by ATR-FTIR spectroscopy.

## MATERIAL AND METHODS

To monitor the colour changes during the steaming there were used the beech dimension timbers with dimensions  $27 \times 75 \times 320$  mm, which were treated by saturated water vapour in a pressure autoclave APDZ 240 under the regime, which is shown in Fig. 1. They were subsequently dried to moisture  $12.0 \pm 0.5\%$  and the loading areas were treated in a horizontal milling machine FS 200.



**Fig. 1 Regime of thermal treatment of beech wood using saturated water steam (DZURENDA 2014).**  $t_{\max} = 115$  °C,  $t_{\min} = 110$  °C,  $t_4 = 100$  °C,  $\tau_1 = 4.5$  h,  $\tau_2 = 1.0$  h.

The surface colour of the samples of original beech wood and steamed beech wood was determined by colourimeter Color Reader CR-10, which is defined by the coordinates of CIE  $L^*a^*b^*$  colour space ( $L^*$ ,  $a^*$ ,  $b^*$ ). To determine the total colour difference  $\Delta E^*$  we used this relationship:

$$\Delta E^* = \sqrt{(L_2^* - L_1^*)^2 + (a_2^* - a_1^*)^2 + (b_2^* - b_1^*)^2} \quad (1)$$

Where  $(L_2^* - L_1^*)$  change in value of black-white coordinate (lightness)  
 $(a_2^* - a_1^*)$  change in value of green-red coordinate  
 $(b_2^* - b_1^*)$  change in the value of blue-yellow coordinate

The average values of colour coordinates  $L^*$ ,  $a^*$ ,  $b^*$  were calculated as arithmetic mean of 40 measurements valid for 95% variability limit.

The surface of the beech dimensional timbers was also analyzed by FTIR on a Nicolet iS 10 spectrometer (Thermo Fisher Scientific) using technique ATR-FTIR on the diamond crystal. The spectra were acquired by accumulating 64 scans at a resolution of  $4 \text{ cm}^{-1}$  in an absorbance mode (A) at wavenumbers from  $4000$  to  $650 \text{ cm}^{-1}$ . Spectral peaks were measured using OMNIC 8.0 software (Thermo Fisher Scientific). Measurements were performed on four replicates per sample. The chemical changes on the wood surface were characterized by the evaluating of average spectra.

## RESULTS AND DISCUSSION

The surface brightness of the sample was visibly changed by the steaming and the sample acquired a different shade. The colour change was objectively characterized by the determining the colour space coordinates  $L^*$ ,  $a^*$  and  $b^*$  in CIE  $L^*a^*b^*$  colour space. Their numerical values were measured on the colourimeter Color Reader CR-10 and compared to each other.

KUBOVSKÝ and URGELA (2004) showed the relevance of the colour matching in practice based on the obtained numerical values of the colour space coordinates. In this way it is possible to determine the conformity of the colours or the colour differences in comparison to a standard.

Table 1 shows the average in value of the lightness of the monitored beech sample surfaces.

**Tab. 1 Effect of steaming on the lightness  $L^*$  and the total colour difference  $\Delta E^*$ .**

Beech wood	Original sample	Steamed sample
Lightness $L^*$	$66.5 \pm 0.14$	$68.6 \pm 0.29$
Total colour difference $\Delta E^*$	3.8	

The lightness of the original beech wood under the influence of the steaming increased from 66.5 to 68.6, representing an increase by 3%. This increase was measured objectively, despite the visual feeling of the darkening sample, due to the changes in other colour space coordinates. KLEMENT and HURÁKOVÁ (2016) also indicate an increase in the lightness of the tangential unreacted sample of beech wood in hydrothermal treatment by the hot air drying.

According to the authors (SOLÁR 1997, MELCER *et al.* 1989), the mechanism of the origin of the colour changes is complicated and a lot of different reactions of basic wood components and their degradation products participate in it. The wood colour change in the hydrothermal treatment is influenced by the reactions of the degradation products of the wood substance and also by the chemical changes of extractives and lignin.

Fig. 2 shows the change of the red-green coordinate  $a^*$  and yellow-blue coordinate  $b^*$  of the colour space CIE  $L^*a^*b^*$  determined on the surface of beech wood due to the steaming.

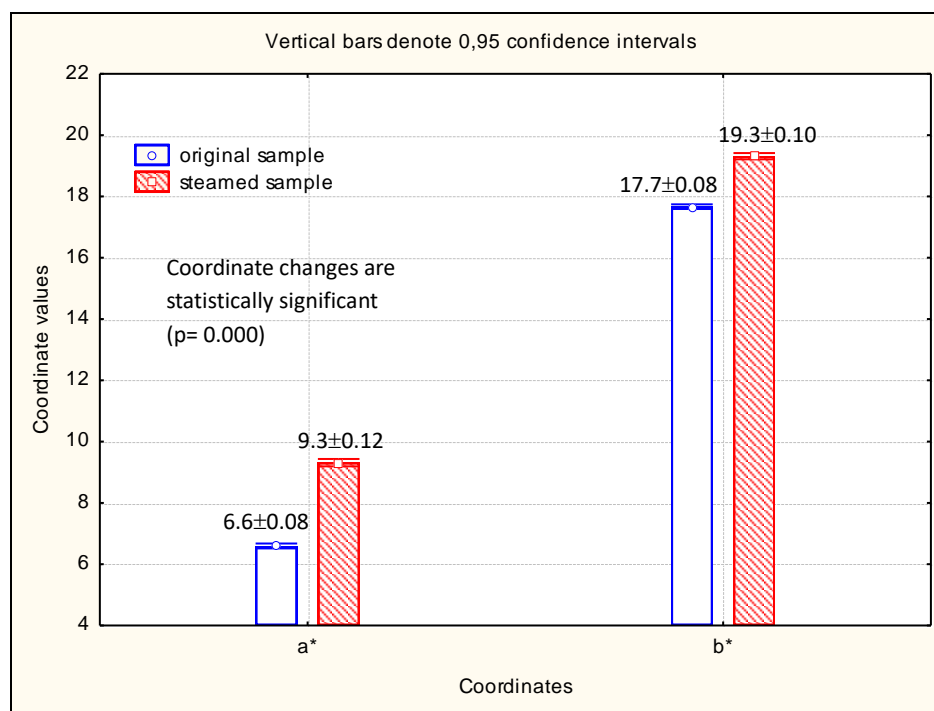


Fig. 2 The effect of steaming on the coordinates of the colour space  $a^*$  and  $b^*$ .

Based on the measured values it can be concluded that the green-red colour space and coordinate  $a^*$  moved due to the steaming from an average of 6.6 to 9.3 towards the red area and its increase amounted to 41%. Blue-yellow coordinate  $b^*$  shifted towards the yellow region of the colour space by 9% compared to the original value. Clearly these changes were confirmed by the visual monitoring too. The surface of the steamed wood had a rosier shade with regard to the original sample.

An important characteristic for monitoring of the colour changes is the total colour difference ( $\Delta E$ ). KUBOVSKÝ and URGELA (2004) consider the colour difference to be a parameter of the major importance in comparing the colours.

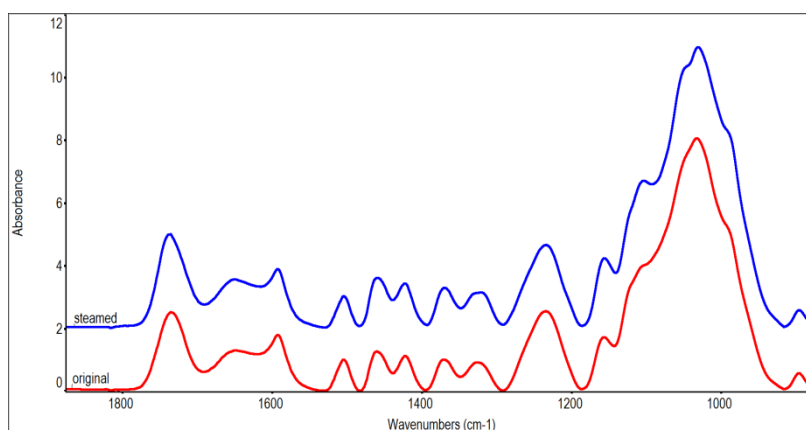
The total colour difference  $\Delta E$  calculated according to the equation (1) for the change of surface colour of beech wood due to the steaming reached the level 3.8. By ALLEGRETTI *et al.* (2009) range  $3 < \Delta E < 6$  can be characterized as "the colour difference visible with a medium quality screen."

The works of many authors (SOLÁR 2004, GEFFERTOVÁ *et al.* 2016, MALEŠIČ *et al.* 2005, MÜLLER *et al.* 2003, STACHOWIAK-WENCEK *et al.* 2015) show, that the surface of the lignocellulosic material changes its colour due to external factors and the resulting colour shade is the result of the complex chemical changes of extractives, polysaccharides and lignin.

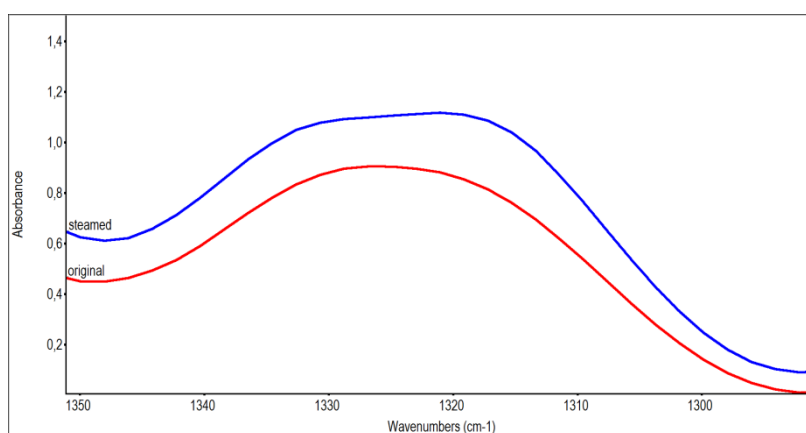
The changes on the beech wood surface, which occurred as a result of the steaming, were studied by ATR-FTIR spectroscopy. The spectra of the original and steamed beech wood are depicted in Fig. 3. They are presented in the fingerprint region ( $1800$  to  $800$   $\text{cm}^{-1}$ ), where most of the specific vibrations occurred.

When interpreting FTIR spectra according to the authors COLOM *et al.* (2003), PANDEY and PITMAN (2003), HON *et al.* (2000), KUBOVSKÝ and KAČÍK (2004), TIMAR *et al.* (2016)

were identified the absorption bands and were associated with the pertaining functional groups, respectively fragments of molecules as follows:  $1736\text{ cm}^{-1}$  for unconjugated C=O groups, mostly present as acetyl groups in xylans;  $1640\text{ cm}^{-1}$  for conjugated C=O and absorbed O–H;  $1593\text{ cm}^{-1}$  for aromatic skeletal vibrations plus C=O stretch;  $1504\text{ cm}^{-1}$  for aromatic skeletal C=C vibrations;  $1459\text{ cm}^{-1}$  for aromatic C–H deformation and asymmetric bending of  $-\text{CH}_3$  and  $-\text{CH}_2-$ ;  $1423\text{ cm}^{-1}$  for C–H deformation in lignin and carbohydrates;  $1370\text{ cm}^{-1}$  for C–H deformation in carbohydrates;  $1335\text{ cm}^{-1}$  for OH in plane bending in cellulose;  $1316\text{ cm}^{-1}$  for  $\text{CH}_2$  wagging;  $1235\text{ cm}^{-1}$  for syringyl ring and C–O stretching in lignin and xylan;  $1157\text{ cm}^{-1}$  for C–O–C asymmetric bridge stretching vibration in cellulose and hemicelluloses;  $1032\text{ cm}^{-1}$  for C–O stretching in cellulose and hemicelluloses; and  $896\text{ cm}^{-1}$  for C–H deformation in cellulose.



**Fig. 3 Comparative FTIR spectra of the surface of steamed and original beech wood in the fingerprint region.**



**Fig. 4 Detail of the FTIR spectra of the surface of beech wood showing the effect of steaming.**

In the spectra of original wood it can be seen at  $1332\text{ cm}^{-1}$  a broad poorly defined main band with an accompanying shoulder. According to COLOM *et al.* (2003) when the crystallised cellulose I and/or II content is increased, this band is gradually converted into a perfectly defined doublet. The doublet at  $1332\text{--}1316\text{ cm}^{-1}$  is assigned to the cellulose component, and is related to the contents in the crystallised and amorphous cellulose. The ratio of intensities  $1332/1316\text{ cm}^{-1}$  can be used to monitor the degradation process. A decrease in the ratio  $1332/1316\text{ cm}^{-1}$  signifies an increase in the crystallinity. In our work we observed a 6.2 % decrease due to the steaming (Fig. 5).

The increase of the crystallinity is obvious from the increase of the total crystallinity index (TCI) too. The absorption band at  $1370\text{ cm}^{-1}$  is an expression of the deformation vibration of C-H in cellulose and hemicelluloses. Band at  $2900\text{ cm}^{-1}$  corresponds to valence vibration of -CH in -CH<sub>2</sub>- and -CH<sub>3</sub> groups. The ratio of their absorbances is the total crystallinity index (O'CONNOR *et al.* 1958). TCI value increased by the steaming from 1.36 to 1.54, i.e. relatively increased by 13.2 % (Fig. 5). This is probably due to the partial degradation of hemicelluloses and amorphous cellulose regions by the influence of heat.

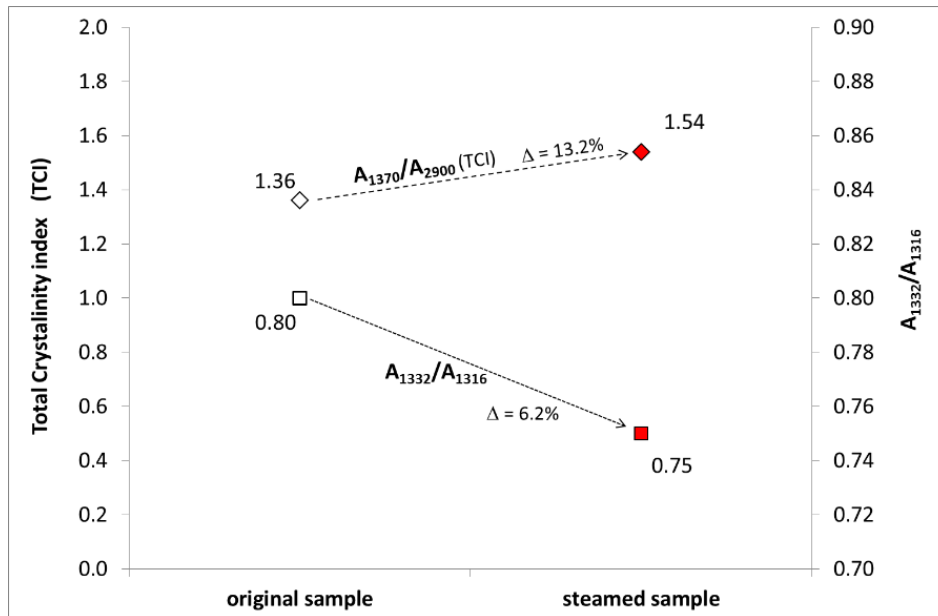


Fig. 5 Effect of steaming on TCI and ratio  $A_{1332}/A_{1316}$ .

Fig. 6 shows a decrease in ratio  $A_{1370}/A_{1504}$  from 0.94 to 0.84 (i. e. the decrease by 10.6 %) during the steaming. This decrease also points to the degradation of polysaccharides. Hemicelluloses are the most degradable constituents of wood. According to FENGL and WEGENER (1984), beech wood contains 19 % of xylose. The hydrolysis of xylan starts with deacetylation of esterified hydroxyl groups, that contribute to a decrease in the ratio of intensities 1736/1640 (non-conjugated carbonyl/ conjugated carbonyls).

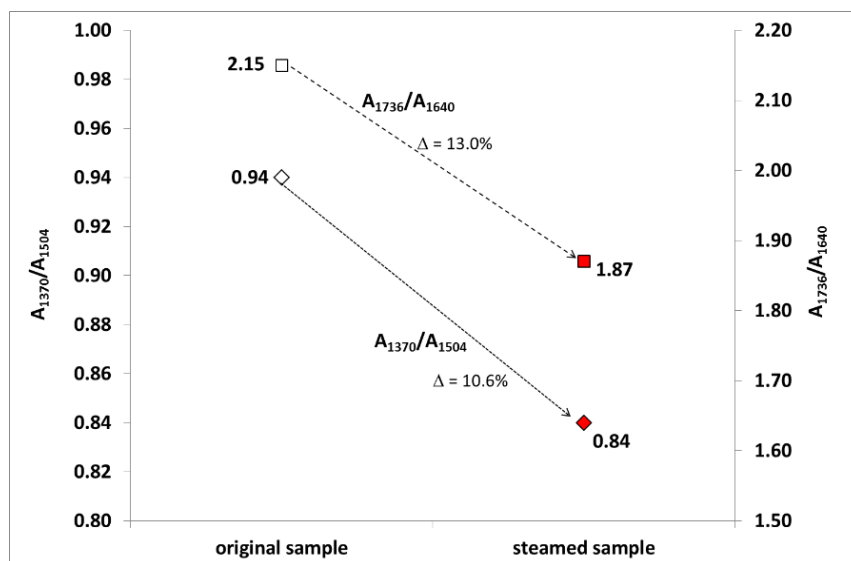


Fig. 6 Effect of steaming on ratio  $A_{1736}/A_{1640}$  and ratio  $A_{1370}/A_{1504}$ .

## CONCLUSION

The influence of the steaming led to an increase of the lightness by 3% compared to the original sample of beech wood. A shift coordinate  $a^*$  due to the steaming was to the red area of the colour space and the shift coordinate  $b^*$  was to the yellow area. Green-red coordinate  $a^*$  moved by the steaming into the red area and its increase amounted to 41%, blue-yellow coordinate  $b^*$  shifted towards to the yellow region by 9% compared to the original value. The overall colour difference  $\Delta E$  due to the steaming can be characterized as "the colour difference visible with a medium quality screen".

The colour changes of beech wood due to the steaming are the result of the complex chemical changes of the wood components. A decrease in the ratio of intensities  $1332/1316\text{ cm}^{-1}$  and an increase of TCI value by the steaming signifies an increase in the crystallinity of cellulose. A decrease in ratio  $A_{1370}/A_{1504}$  points to the degradation of polysaccharides during the steaming.

The steaming causes the partial degradation of the hemicelluloses and amorphous cellulose regions. It is accompanied with the concomitant release of lignin-carbohydrate bonds in the surface layers of wood, which is reflected in the subsequent removal of the easily degradable polysaccharides and in relative increase of the lignin content.

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